Atmospheric Concentrations of Polycyclic Aromatic Hydrocarbons and Nitro-PAHs: Gas- particle partitioning and possible sources at Rural and Traffic site of Agra

A Synopsis

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INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) belong to one of the class of anthropogenic air pollutants. They enter in the environment as a result of a number of anthropogenic and natural activities (Chong *et al*., 2015; Birgul and Tasdemir, 2015). PAHs are mainly formed as a result of pyrolytic processes such as petroleum refining, chemical manufacturing, air blowing for asphalt, emissions from coal, oil, gas and wood refuse incineration for cooking and heating, biomass burning, power generation and vehicle emissions (Nadal *et al*., 2004; Durand *et al*., 2004). The contribution from natural sources of PAHs is limited, being restricted to spontaneous forest and prairie fires and volcanic emissions (Bourotte *et al*., 2005). Emissions of PAHs vary with combustion systems; the large-scale combustion, e.g., industrial with a burning rate of hundreds kilograms per hour, is normally better controlled, more complete, and results in lesser formation of PAH than small-scale combustion such as domestic cook stoves with a burning rate of a few hundred grams to a few kilograms per hour. For example, the emission factor of Benzo[*a*]Pyrene, a well established carcinogenic PAH from small-scale wood stoves can exceed that from coal on an energy equivalent basis with a factor of 100. PAHs are considered highly toxic for human beings and several of these compounds are carcinogenic, mutagenic or teratogenic (Santos *et al*., 2002; Kavouras and Stephanou, 2002). Due to their toxic, mutagenic and carcinogenic properties, 16 PAHs have been identified as priority pollutants by United States Environmental Protection Agency (USEPA) and seven of them are considered as some of the strongest known carcinogenic compounds (IARC, 1991). They are of special interest due to their toxicity, carcinogenicity, and ubiquitous presence in the environment (Chong *et al*., 2015; Birgul and Tasdemir, 2015; Mc Crillis *et al*., 1992).

PAHs can be formed by both pyrolysis and pyrosynthesis. At high temperatures greater than 500^{o}C, carbon–carbon and carbon–hydrogen bonds of organic compounds are ruptured, resulting in the formation of reactive free radicals. These radicals further combine and then condense to form

aromatic ring structures, which are resistant to thermal degradation. These PAHs are less alkylated and contain more aromatic rings than petrogenic PAHs (Hwang *et al*., 2003). The tendency of hydrocarbons to form PAHs by pyrosynthesis is highest for aromatics and decrease gradually for cycloolefins, olefins, paraffins in the same order (Manahan, 1994).

On the basis of molecular weights, PAHs are classified into three categories, which are low, medium and high molecular weights PAHs. 2-3 ring PAHs and those whose molecular weight ranges up to l78 g/mol are Low Molecular Weight PAHs (LMW) e.g., Naphthalene, Phenanthrene. The 4 ring PAHs are called Medium Molecular Weight (MMW) PAHs and their molecular weight ranges between 202-228 g/mol e.g., Fluoranthene and Pyrene. The third class of PAHs is High Molecular Weight (HMW) PAHs, it usually contains 5-7 ring PAHs and their molecular weight ranges between 228 to 278 g/mol e.g., Benzo(a)Pyrene, Dibenzo (a,h) Anthracene and Indeno (1,2,3-cd) pyrene (ATSDR, 1995). Low molecular weight PAHs are generally produced during low temperature burning processes (e.g. wood burning), while high temperature burning processes (e.g. combustion of fuels in engines) generate higher molecular weight PAHs (Mostert *et al*., 2010).

PAHs are semi-volatile organic compounds (SVOCs) and therefore they can exist in both the particulate and gaseous phases (Finlayson-Pitts and Pitts, 2000). PAHs are hydrophobic in nature because of which they tend to bind on the surface particles (Ratola *et al*., 2011) and cannot be easily degraded, they are subjected to long range transport, Hence these are detected in remote areas, where primary emissions are limited (Odabasi *et al*., 1999; Vasilakos *et al*., 2007). PAHs in air, soil and water can be transported from one medium to another by volatilization, evaporation, dissolution, dry/wet deposition, and gas adsorption processes. Therefore, environmental fates of PAHs are strongly dependent on their gas/particle distribution (Offenberg and Baker, 2002; Mastral *et al*., 2003; Gaga *et al*, 2009).

The partitioning of PAHs between gas and particulate phases depends mainly on the compound's subcooled liquid vapor pressure, particle characteristics like size distribution, chemical composition, and carbon content and atmospheric conditions like temperature and relative humidity (Sitaras *et al*., 2004; Esen *et al*., 2008). Gas/particle partitioning include surface adsorption on ambient particles and adsorption in liquid organic layer of particles. Low molecular weight PAHs are found mostly in vapour phase, while MMW and HMWs are found mainly adsorbed on particulate material (Park *et al*., 2002). The concentration of each component in these phases is a function of the volatility and affinity to the surface of atmospheric particles.

Gas/particle partitioning can be quantified by a gas/particle partition coefficient, K_p (m^3 μg^{-1}) which can be expressed as

$$Kp = \frac{Cp}{Cg} \quad \text{(Cotham and Bidleman, 1995; Gustafson } et\ al\text{., 1997)} \qquad (1)$$

The fraction (ϕ) of compound in the particle phase is

$$\phi = Cp\frac{(\text{TSP})}{[Cg + Cp\ (\text{TSP})]} = Kp\frac{\text{TSP}}{[1 + Kp\ (\text{TSP})]} \qquad (2)$$

where C_p is the concentration on particles (ng μg^{-1} of particles), C_g is the gas-phase concentration (ng m^{-3} of air), and TSP is the total suspended particle concentration ($\mu g\ m^{-3}$). Gas/particle partition coefficient can be correlated with subcooled liquid vapor pressure ($p°_L$) of PAHs using the following equation

$$\log K_p = m \log p°_L + b \qquad (3)$$

the expected slope (m) of equation (3) is -1 under equilibrium conditions. Interpretation of the intercept term (b) depends on the assumed mechanism of particle-gas interaction. If compounds are adsorbed to active sites on the particle surface, b is related to the specific surface area of the particle and the excess heat of desorption from the particle surface (Pankow, 1987; Pankow, 1991). If the

mechanism is absorption into a liquid like film on the aerosol, *b* depends on the fraction of organic matter in the particle that is involved in the partitioning process and the activity coefficient of the compound in the organic film (Pankow, *1994a*). Various models have been proposed to explain the gas/particle partitioning of semi-volatile compounds. The *Junge-Pankow Adsorption Model,* first proposed by Junge (Junge, 1977) and later critically reviewed by Pankow (Pankow, 1987), assumes that chemicals adsorb to active sites on the surface of the particle. The Junge-Pankow model (equation 4) is the most common method for estimating adsorption of semi-volatile organic compounds to aerosols.

$$\phi = \frac{c\theta}{(p°_L + c\theta)} \quad (4)$$

This model relates the fraction of chemical adsorbed to particles (ϕ) to the subcooled liquid vapor pressure of the pure compound ($p°_L$, Pa) and the particle surface area per unit volume of air (θ, cm^2 of aerosol cm^{-3} of air). The parameter *c* (Pa cm) is based on the heat of desorption from the particle surface, the heat of vaporization of the compound, and the moles of adsorption sites on the aerosol. A value of c = 17.2 Pa cm is typically used, although Pankow (Pankow, 1987) suggests that this may vary with the class of compound. Values for the surface area parameter, θ, are often assumed to be 1.1 x 10^{-5} for urban air and (4.2-35) x 10^{-7} for rural air (Bidleman, 1977). An alternate *Absorption Model* proposed by Pankow (Pankow, 1994a, 1994b) considers that atmospheric aerosols are coated with organic film, into which the absorption of the chemical takes place. Pankow's expression for K_P based on absorption is

$$Kp = 10^{-6} RT f_{om} / M_{om} \Upsilon om\, p°_L \quad (5)$$

where f_{om} is the fraction of the particle mass that consists of absorbing organic matter having molecular weight M_{om} (g mol^{-1}) and activity coefficient Υ_{om} in the organic film. A substantial portion of this organic matter may be secondary organic aerosol, which is formed by oxidation of hydrocarbons that is polar in nature (Pankow, 1994b). A problem with the absorption model is that

Υ_{om} is not often known, and may vary substantially among different classes of compounds (Liang and Pankow, 1996; Jang *et al*., 1997)

K_{OA} *Absorption Model*. PAHs are hydrophobic in nature. Writing equation 5 in the logarithmic form,

$$\log Kp = \log f_{om} + \frac{\log 10^{-6} RT}{M_{om}\, \Upsilon_{om}\, p°_L} \qquad (6)$$

where the term $\log 10^{-6} RT / M_{om}\, \Upsilon_{om}\, p°_L$ is related to the partition coefficient of the compound between the organic matter and air. Thus the octanol-air partition coefficient (K_{OA}) can be used as an alternative to vapor pressure for describing absorption to aerosols (Finizio *et al*., 1997; Harner and Bidleman, 1996; Harner and Mackay, 1995). Values of K_{OA} have been reported as a function of temperature for several PCB congeners, chlorobenzenes, PAHs, and polychlorinated naphthalenes (PCNs) (Harner and Bidleman, 1996, 1998; Harner and Mackay, 1995).

The relationship between K_P and K_{OA} is (Finizio *et al*., 1997; Bidleman and Harner, 1997c)

$$K_P = 10^{-9}\, K_{OA}\, f_{om}\, (\Upsilon_{oct} / \Upsilon_{om})\, (M_{oct}/M_{om}) / \rho_{oct} \qquad (7)$$

where f_{om} is the fraction of organic matter in the aerosol involved in partitioning, Υ_{oct} and Υ_{om} are the activity coefficients of the absorbing compound in octanol and aerosol organic matter, M_{oct} and M_{om} are the molecular weights of octanol (130 g mol^{-1}) and the organic matter, and ρ_{oct} is the density of octanol (820 kg m^{-3}). With the assumptions that $\Upsilon_{oct} / \Upsilon_{om}$ and $M_{oct} / M_{om} = 1$:

$$\log Kp = \log K_{OA} + \log f_{om} - 11.91 \qquad (8)$$

The K_{OA} absorption model (equation 8) can be used to predict values of K_P from knowledge of only K_{OA} and the organic fraction of the aerosol, f_{om}, if it is further assumed that all of the aerosol organic matter is available to absorb gaseous compounds. The fraction on particles (ϕ) is then calculated from K_P and TSP by equation 2.

Particulate bound PAHs can be subject to chemical transformation through gas-particle interactions occurring either in exhaust systems, stacks, emission plumes, or during atmospheric transport resulting in decrease in concentration in the atmosphere. PAHs may undergo

1) photochemical modifications under irradiation from different sources.

2) non-photochemical degradation (spontaneous oxidation in the dark).

3) chemical modifications induced by reactions between atmospheric gases (NOx, SOx, O_3) and various PAH adsorbed onto different substrates, in the absence or the presence of radiation. PAHs can react with molecular oxygen in absence of irradiation, but speed of such reactions is very slow and they have no considerable effect on total degradation process. Ozone is an important gaseous pollutant influencing PAHs concentration (Valerio *et al*., 1984). Ozone concentrations occurring in natural conditions lead to considerable decrease of half life of PAHs. Reactions with the ozone and free radicals have the most important influence on concentration of PAH in gaseous phase.

In the atmosphere unsubstituted PAHs react with NO_2 and HNO_3 and are transformed into to their nitro-derivatives (Nielsen, 1984). Nitro-PAHs are also formed from incomplete combustion processes or by the reaction of PAH with atmospheric oxidants, such as dinitrogen pentoxide, nitrogen trioxide, and oxygen radicals in the presence of nitrogen oxides (Enya *et al*., 1997; Environmental Health Criteria–EHC, 2003). As the nitro-PAH isomers are produced through both direct and secondary sources, some researchers have used nitro-PAHs as tracers for vehicular emissions or gas-phase reactions in ambient samples (Ciccioli *et al*., 1996; Feilberg *et al*., 2000; Marino *et al*., 2000). Nitro-PAHs formed in stack and exhaust gases (such as 1-nitropyrene and 3-nitrofluoranthene) which undergo electrophilic reactions in the presence of NO_2 to form nitro-PAH in the plume gases after combustion but before extensive dilution after emission occurs (Nielson, 1984). However gas phase reactions of the parent PAH with the OH or NO_3 radicals results in to the formation of 2-nitrofluoranthene and 2-nitropyrene (Zielinska *et al*., 1986).

Nitrated polycyclic aromatic hydrocarbons (N-PAHs) have been recognized as direct-acting mutagens and carcinogens to mammalian systems and are, thus, considered to have far greater toxicity than unsubstituted PAHs (Chong *et al.*, 2015; Huang *et al*., 2014; Bandowe *et al*., 2014; Atkinson and Arey, 1994). PAHs have been investigated extensively in the ambient air, while the derivatives of PAHs such as nitro and hydroxyl have received less attention in spite of their higher toxicity than their parent PAHs. Nitro- and oxy-PAHs in very low concentrations have been detected in ambient atmosphere as compared to their parent PAHs. In semi-rural and urban atmospheres, detectable levels of nitro-PAH and oxy-PAH have been found (Feilberg *et al*., 2001). Nitro-PAHs are highly persistent in the environment and can be transported long distances from their original source (Nielson *et al*., 1984; Ciccioli *et al*., 1996). The increased attention to nitro-PAHs, particularly in the environmental analytical community, is due to their persistence in the environment and higher mutagenic ($2x\ 10^5$ times) and carcinogenic (10 times) properties of certain compounds compared to PAHs (Lewtas *et al*., 1990; Durant *et al*., 1996). In IOMEH (Institute of Occupational Medicine and Environmental Health), the mutagenic activity of PAHs and nitro-PAHs fractions was studied. This study showed that nitro-PAHs fraction exhibit higher mutagenic activity. Nevertheless, the concentrations of nitro-PAHs were ten times lower in comparison to PAHs. Therefore a need to measure low concentrations of nitro-PAHs in the air exists because even in such concentrations these compounds can cause health hazard (Tsapakis and Stephanou, 2005).

PAHs also undergo photodecomposition. Few studies indicate that PAH in the vapour phase are more susceptible to such reactions than those associated with particulates (Kamens *et al*., 1988; Valerio *et al*., 1984; Wild *et al*., 1995). Thus adsorption on highly porous, carbonaceous particles like soot or fly-ash may provide some protection from photo oxidation (Nielsen *et al*., 1984). Kamens *et al*., 1988 found that at moderate temperatures the rate of PAH photodecomposition may decrease with increased PAH particle loadings. Seasonal variation in transformation reactions of PAHs have been observed. During winter, with conditions of low temperature and low irradiation,

the major pathway for PAH degradation is probably reactions with nitrogen oxides, sulfur oxides and with the corresponding acids. During winter PAHs concentrations are higher compared with those during summer. This can be ascribed to one or more of the following reasons:

1) The gas–particle distribution changes towards the gas phase at higher temperatures.

2) Degradation of PAHs increases with increasing solar flux.

3) Emissions could be higher in the winter due to cold engine conditions.

Which of the three factors is dominating depends on compound properties, such as photostability, volatility, formation mechanism (petrogenesis or pyrogenesis) etc. In general, low-volatile PAHs with > 5 rings, characterized by relatively high temperature of condensation, are adsorbed on the airborne particles (Van jaarsveld *et al*., 1997). They are classified in the low mobility category of PAHs subjected to rapid deposition and retention close to the source (Wania *et al*., 1996). The lower-molecular weight compounds with 2-3 rings, exhibiting low temperatures of condensation, are more abundant in the gas phase (Subramanyam *et al*., 1994; Valerio *et al*., 1984; Van jaarsveld *et al*., 1997; Wania *et al*., 1996; Wild *et al*., 1995).

PAHs may also be removed from the atmosphere by dry deposition (Seinfeld *et al*., 1997). The factor that governs dry deposition is turbulence, chemical properties of the compound, and the nature of the surface to which deposition takes place (Seinfeld *et al*., 1997). Dry deposition of gaseous PAH to vegetation either occurs via equilibrium partitioning between the gas phase and the vegetation or via kinetically limited gaseous deposition (McLachlan *et al*., 1999). The equilibrium partitioning is highly dependent on the properties of the compound, but also depends on the nature of the vegetation surface (Bohme *et al*., 1999). The average dry deposition velocity of particulate PAHs has been estimated recently to be 6.7, 2.8 cm/s (Odabasi *et al*., 1999) for a series of PAHs. The smallest deposition velocities are observed for particle diameters ranging from ~0.1 to ~1 μm (Seinfeld *et al*., 1997) and, interestingly, many PAHs are also found to be associated with particles of this size. PAHs and nitro-PAHs have been observed to be absorbed into tree bark (Douce *et al*.,

1997) and pine needles (Tremolada *et al*., 1996) and are also deposited to forest canopies (Horstmann *et al*., 1998; Simonich *et al*., 1994) used a mass balance model to estimate the removal of PAHs to vegetation. The model predicted that 18 % of PAHs emitted into the atmosphere in a specific region was removed by vegetation. Both particle and gas phase dry deposition are believed to contribute to the presence of PAHs in vegetation.

Once released into the atmosphere, many PAHs and nitro-PAHs are highly persistent in the environment and can be transported long distances from their original source (Ciccioli *et al.*, 1996). The increased attention to nitro-PAHs, particularly in the environmental analytical community, is due to their persistence in the environment and higher mutagenic and carcinogenic properties of certain compounds compared to PAHs. Although at lower concentrations compared to unsubstituted parent PAHs, in recent years it has become well-established that certain nitro-PAHs exhibit high direct-acting mutagenic potency in a microbial mutagenicity bioassays and in a forward mutation assay based on human cells. Furthermore, nitro-PAHs can be a significant fraction of the direct-acting mutagenic compounds present in extracts of ambient air particles (Wang *et al*., 1980) and their persistence in the particulate phase may result in human exposure through inhalation. These concerns have stimulated research into the primary sources, fate, and transport of these contaminants in the atmosphere. However, typical atmospheric particulate concentrations of nitro-PAHs are in the low ng/g level. Certain nitro-PAH isomers are produced through either direct or secondary sources; some researchers have used nitro-PAHs as tracers for vehicular emissions or gas-phase reactions in ambient samples (Marino *et al.*, 2000). Therefore, identification of isomeric nitro-PAHs is necessary to characterize the direct versus secondary sources of nitro- PAHs. A lack of information still exists about NPAH levels in the atmosphere in India, in particular, no measurements of NPAH have been yet made in India, although PAH were monitored since late eighties.

LITERATURE REVIEW

In recent years, a number of studies on PAHs have been conducted in various cities of the world. These studies identified and quantified several PAH compounds in samples collected from the air environment (Li *et al*., 2005), and from direct emission of several sources such as domestic combustion (Li *et al*., 2003), natural gas combustion in residential appliances, tobacco smoke (Ding et al., 2005) and gasoline and diesel vehicle exhaust (Zielinska *et al*., 2004; Yang *et al*., 2010). Gas–particle partitioning of PAHs has also been extensively studied in different urban, remote, and coastal environments around the world (Cotham and Bidleman, 1995; Dachs and Eisenreich, 2000; Fernandez *et al*., 2002; Sitaras *et al*., 2004; Tsapakis and Stephanou, 2005; Tasdemir and Esen, 2007; Akyuz and Cabuk, 2010). It is also alarming to note that annual PAH emissions from Asian countries were 290 Gg year^{-1}, with China and India contributing 114 and 90 Gg year^{-1}, respectively. The proportion of high molecular weight PAH emission from India (3.60%) was significantly higher than the global average. Large amount of data on concentration levels of SPM, NO_x, SO_2 and CO are available for prominent urban areas in India, studies on measurements of PAHs in the ambient air of major cities are rather limited. The studies so far conducted are on PAH composition in only the respirable suspended particulate phase (Pandit *et al*., 1996; Chattopadhyay *et al*., 1998; Kulkarni 1997, Kulkarni and Venkataraman, 2000; Sharma *et al*., 2008; Rajput *et al*., 2009, 2010; Mohanraj and Azeez, 2004; Mohanraj et al., 2011a, 2011b; Rajput and Lakhani, 2009, 2010, 2012; Jain et al., 2012; Singla et al., 2012; Lakhani, 2012; Dubey *et al*., 2014) and gas phase PAHs have been rather neglected. No study on gas-particle partitioning of neither PAHs nor the levels of derivatives of PAHs has yet been reported.

The gas-particle partitioning behavior of polycyclic aromatic hydrocarbons has been evaluated in several urban sites like in Xi'an, central China (Chong *et al*., 2015), Bursa (Turkey) at four different sites (Birgul and Tasdemir, 2014), Quanzhou and Xiamen, two cities in southern part of China (Wu *et al*., 2014), Dalian (Zhou *et al*., 2013), sites near the Yellow sea (Wang *et al*., 2013), sites in the

Chinese Northern plains (Yang *et al*., 2010) Guangzhou City (Liu *et al*., 2009) in China by simultaneous monitoring of PAHs in both gas and particulate phases. The observed concentrations of atmospheric PAHs were generally higher than those reported for developed countries PAHs displayed seasonal variation in the order of winter > autumn > spring > summer. PAHs were much higher during the heating period than non heating period. PAHs in gas phase were all higher than those in particle phase in the four seasons. The gas-particle partitioning mechanisms of PAHs were influenced by ambient temperature; in the colder ambient, both adsorption and absorption mechanism dominate the partitioning mechanisms, while in relative warmer ambient, absorption mechanism contributed more to the partitioning process. Pine (*Pinus thunbergii*) needles and surface soils were simultaneously sampled at 35 sites across Liaoning province, China, to investigate the distribution of polycyclic aromatic hydrocarbons (PAHs) in the two media (Wang *et al*., 2011).

Concentration of PAHs in the indoor and outdoor air of schools was determined. The sampling was done at five primary schools in the city of Kaunas Lithuania during the heating season of 2011/2012. In the entire sampling period 150 daily samples of particulate and vapor phases were collected. The concentration of total PAHs in the $PM_{2.5}$ fraction ranged from 20.3 to 131.1 ng m^{-3}, while total suspended particles (TSP) fraction contained from 19.9 to 80.3 ng m^{-3} of total PAHs. The vapor phase concentration of PAHs ranged from 67.2 to 372.5 ng m^{-3}.Napthalene was determined as the dominant PAHs in both the phases. The analysis revealed that emissions from motor vehicles and fuel burning for heating purposes were the major sources of PAHs in the city of Kaunas (Krugly *et al*., 2014).

In Madrid (Spain), the concentration of PAHs and their substituted derivatives from January 2008 to February 2009 in a suburban area of a large city were reported (Barrado *et al*., 2013). In this

study 13 PAHs, 5 nitro-PAHs and 2 hydroxy-PAHs in 55 vapor-phase samples were analyzed. Seasonal trends and correlations between the concentrations of these compounds and a series of meteorological factors (e.g., temperature, atmospheric pressure) and physical–chemical factors (e.g., nitrogen and sulfur oxides) was also observed in the atmospheric pollutants. A ‘‘mean sample’’ for the 14-month period would contain a total PAH concentration of 13835 ± 1625 pg m^{-3} and 122 ± 17 pg m^{-3} of nitro-PAHs. The concentration in the coldest month was calculated 18900 ± 2140 pg m^{-3} for PAHs and 150 ± 97 pg m^{-3} of nitro- PAHs, while in an average sample collected in the warmest months, these values drop to 9293 ± 1178 pg m^{-3} for the PAHs and to 97 ± 13 pg m^{-3} for the nitro-PAHs. Total vapor phase concentrations of PAHs were one order of magnitude higher than concentrations detected in atmospheric aerosol samples collected on the same dates. Total nitro-PAH concentrations were comparable to their aerosol concentrations whereas vapor phase OH-PAHs were below detection limits, indicating that these were trapped in airborne particles.

Gas and particle-phase ambient air samples were collected at a traffic site in Eskisehir over a six-month period between January and October 2006. Gas-particle concentrations of 15 PAHs were determined by analyzing integrated glass fiber and polyurethane foam samples. On average, 66% of the total concentrations of PAHs were found in the gas-phase in heating and 69% in the non-heating period samples. Heating period PAH concentrations were found to be 7 to 8 times greater than concentrations in non-heating period samples. Multiple linear regression analysis was carried out to determine the effect of meteorological parameters on measured individual PAH concentrations. Temperature, wind speed and wind direction explained 43% (Dibenzo[a,h]Anthracene and Benzo[a]Pyrene) to 78% (Phenanthrene) of the variability in atmospheric PAH concentrations. Results of the multiple linear regression analysis indicated that temperature and wind speed were statistically significant factors for the measured concentrations of PAHs. Gas–particle partitioning coefficients, (*Kp*) and particle phase fractions (Φ) of PAHs, were correlated with supercooled vapor

pressures ($p°_L$). Application of non-linear fitting for Φ versus log $p°_L$ ts was found to be more robust than linear logarithmic regressions of log *Kp* versus log $p°_L$. Particle-phase fractions (Φ) for each PAH were also calculated using octanol–air and soot–air partitioning models. Soot model resulted better predictions of Φ for Fluorene, Phenanthrene, Anthracene, Fluoranthene and Pyrene. Both two models yielded very similar particle-phase fractions having very close results to experimentally obtained Φ values for the rest of PAHs measured (Gaga *et al*., 2011). PAHs were measured in the rural atmosphere of Southern Ontario, Canada from October 2001 to November 2002. Gaseous and particle-bound concentrations of PAHs were determined concurrently in a forest and a clearing. The gas-particle partitioning behavior of the PAHs was investigated by fitting the original Junge-Pankow equation to the fraction in the particle phase for each set of measured data. The magnitude of the differences in the model fitting parameters between sampling events was consistent with the reported variability in the nature and concentration of atmospheric particles. Statistical tests on the regression results indicate that the gas-particle partitioning was not significantly different between the forest and the clearing (Su *et al*., 2006).

The global atmospheric distribution and long-range transport (LRT) potential of three polycyclic aromatic hydrocarbons (PAH) – Anthracene, Fluoranthene and Benzo[a]Pyrene were studied through a global aerosol-chemistry-transport-model, which is based on an atmospheric general circulation model. The results showed that PAHs are mostly distributed in the source regions but reach the Arctic and the Antarctic. The Canadian Arctic is predicted to be significantly less affected by mid-latitude PAH emissions than the European Arctic. Re-volatilisation is significant for semi-volatile PAHs. Accumulation of semi-volatile PAHs in polar regions, however, is not indicated. The model study suggests that gas/particle partitioning in air drastically influences the atmospheric cycling, the total environmental fate (e.g. compartmental distributions) and the LRT potential of the substances studied. A parameterisation which calculates the gas-particle partitioning assuming absorption into organic matter and adsorption to black carbon (soot) agrees best with the

observations at remote sites. The study provides evidence that the degradation in the particulate phase must be slower than that in the gas-phase. The predicted concentrations of the semi-volatile PAHs Anthracene and Fluoranthene in near-ground air at remote sites in mid and high northern latitudes are in line with measured concentrations, if adsorption of the substances to soot combined with absorption in particulate organic matter is assumed to determine gas-particle partitioning, but cannot be explained by adsorption alone (Junge–Pankow parameterisation of gas-particle partitioning). The results suggest that PAHs absorbed in the organic matrix of particulate matter is shielded from the gas-phase (Lammel *et al*., 2009). PAHs were measured together with inorganic air pollutants at two urban sites and one rural background site in the Banja Luka area, Bosnia and Hercegovina, with the aim to study gas-particle partitioning, aerosol mass size distributions and to explore the potential of a higher time resolution (4 hour sampling). In the particulate phase the mass median diameters of the PAHs were found almost exclusively in the accumulation mode (0.1 - 1.0 mm of size). These were larger for semi-volatile PAHs than for non-volatile PAHs. Gas-particle partitioning of semi-volatile PAHs was strongly influenced by temperature. The results suggest that the Junge-Pankow model is inadequate to explain the inter-species variation and another process must be significant for phase partitioning which is less temperature sensitive than adsorption.

Ambient air and dry deposition samples were collected at suburban and urban sites in Izmir, Turkey. Atmospheric total (particle + gas) of 14 PAHs concentrations were 36±39 and 144±163 ng m^{-3} for suburban and urban sites, respectively. Phenanthrene was the most abundant compound at all sites, and all samples were dominated by low molecular weight PAHs. Average particulate PAHs dry deposition fluxes were 8160±5024 and 4286±2782 ng m^{-2} day^{-1} and overall average particulate dry deposition velocities were 1.5±2.4 and 1.0±2.3 cm s^{-1} for suburban and urban sites, respectively. Soil samples were collected at suburban site. Average soil concentration for 14PAH was 55.9±14.4 ng g^{-1} dry weight. Calculated gas-phase air–soil exchange fluxes indicated that Fluorene, Phenanthrene, Anthracene, and Carbazole were deposited to soil in winter while they

were volatilized in summer. Other compounds (Fluoranthene-Benzo[g,h,i]Perylene) were deposited to soil in both periods. Annual average fluxes of PAHs representing soil to air (i.e., gas volatilization) and air to soil transfer (i.e., gas absorption, dry deposition, and wet deposition) processes were also compared. All processes were comparable for 14PAHs however their input was dominated by gas absorption. Gas absorption dominated for lower molecular weight PAHs, however dry deposition dominated for higher molecular weight PAHs. The results have suggested that for Fluorene, soil and air may be approaching a steady state condition. For the remaining compounds, there was a net accumulation into the soil (Demircioglu *et al*., 2011). A comprehensive sampling campaign was carried out to study atmospheric concentration of polycyclic aromatic hydrocarbons (PAHs) in Beijing and to evaluate the effectiveness of source control strategies in reducing PAHs pollution after the 29th Olympic Games. Pyrogenic sources and coke oven emission were identified as major sources for both the non-heating and heating seasons. As compared with literatures, the mean PAH concentrations before and after the 29th Olympic Games were reduced by more than 60%, indicating that the source control measures were effective for reducing PAHs pollution in Beijing (Maa *et al*., 2011).

Gas and particle-phase polycyclic aromatic hydrocarbons (PAHs) were measured in air at a background site (Xiaolongmen), two rural village sites (Gubeikou and Donghe), and at an urban site (Beijing) in the North China Plain from September 2007 to August 2008. The annual average total PAH concentration in Donghe was 730.7±608.0 ng m^{-3} and 18.2, 3.0, and 1.8 times higher than Xiaolongmen, Gubeikou and Beijing, respectively. Gas-particle partitioning of PAHs approached equilibrium at the background site (Xiaolongmen) because of long-range transport and longer transport times of the PAHs. Study showed that PAH adsorption onto soot carbon and absorption into organic matter were both important for PAH gas/particle partitioning in the North China Plain (Wang *et al*., 2011).

Atmospheric concentrations and gas–particle partition coefficients were determined for PAHs in the atmosphere of Zonguldak, Turkey between May 2007 and April 2008. Total concentrations of PAHs ranged from 0.52 ng m^{-3} to 636 ng m^{-3} in the particle phase and from 5.60 ng m^{-3} to 725 ng m^{-3} in the gas phase. The annual mean concentrations of PAHs in the particle and gas phase were found to be 114 ng m^{-3} and 184 ng m^{-3}, respectively. Significant seasonal variations of particle and gas phase PAH concentrations were observed with higher levels during cold period. Three ring PAHs were associated primarily with the gas phase, four ring PAHs were distributed almost equally between the two phases and five and six ring PAHs were mainly associated with the particle phase. The relationships between temperature and gas phase partial pressures of PAHs were examined using the Clausius–Clapeyron equation and the obtained positive slopes indicated that PAH concentrations increased with decreasing air temperature as a result of high dominance of local emissions (Akyuz and Cabuk, 2010). Air samples were collected in an urban and industrialized area of Prato (Italy) during 2002, as part of a study to identify and measure aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). Total concentrations of aliphatic hydrocarbons ranged between 170 and 282 ng m^{-3} in the gas phase and from 48.9 to 276 ng m^{-3} in the particulate phase. The average total PAH concentrations (gas + particulate) were 59.4 ± 26.5 ng m^{-3}, and both gas and particulate phase PAH concentrations decreased with increasing temperature. Source identification using diagnostic ratios and principal component analysis identified automobile traffic, in particular, the strong influence of diesel fuel burning, as the major PAH source. Gas-particle partition coefficients (*Kp's*) of n-alkane and PAHs were well correlated with the sub-cooled liquid vapour pressure and indicate stronger sorption of PAHs to aerosol particles compared with n-alkanes. (Cincinelli *et al*., 2007). Atmospheric PAH concentrations were determined in Gulbahce district of Bursa, Turkey between August 2004 and April 2005. The concentrations of total PAHs in heating season were almost ten times higher than those in non-heating season. Diagnostic ratios and factor analysis results show that in the heating season traffic along with residential heating emissions heavily influence PAH concentrations. The $p°_L$ of log *Kp* versus log p^0_L for all the data set of

heating and non-heating season samples gave significantly different slopes. The partitioning results for individual samples further indicated that slope values varied depending on air parcel trajectories. Air parcels traveled over water (either over the Black Sea or Aegean Sea) prior to arriving at the sampling site had less steep slopes. Partitioning of PAHs was also investigated by comparing experimentally determined *Kp* values with the results obtained both from octanol-based model ($Kp_{(Oct.)}$) and soot and octanol-based model ($Kp_{(Soot+Oct.)}$). Both models were useful in predicting the experimental *Kp* values (Esen *et al*., 2008).

Atmospheric concentrations and gas-particle partition coefficients were determined for PAHs in the city of Bursa, Turkey between August 2004 and May 2005. The average total (gas+particle) PAH concentration was 456±524 ng m^{-3}. The ambient air concentrations were mainly influenced by traffic and industrial activities. PAH compounds considered in this study predominantly existed in the gas phase and the average contribution of gas phase to total (gas + particle) PAH concentrations was about 90%. Experimentally determined *Kp* values correlated well with the subcooled liquid vapor pressures (p^0_L) of PAHs. The octanol-air partition coefficient (KOA), which can also be used to calculate *Kp* values, gave high correlation coefficients with the p^0_L. In another approach, the *Kp* values were estimated by considering adsorption onto the soot carbon and absorption into organic matter of atmospheric particulates. In general, *Kp* values calculated based on K_{OA} gave smaller values than the ones predicted based on soot/air (K_{SA}) partition coefficient. Sorption of PAHs on particles was underestimated by K_{OA} suggesting that absorption would not be enough to explain partitioning and adsorption would still be important (Tasedmir and Esen, 2007).

The presence of PAHs in an urban region (Heraklion, Greece) and processes that govern their atmospheric fate were studied from November 2000 until February 2002. The most abundant members (gas+particles) were Phenanthrene, Fluoranthene, Pyrene and Chrysene. Total concentration (gas+particulate) of PAH ranged from 44.3 to 129.2 ngm^{-3}, with a mean concentration of 79.3 ng m^{-3}. Total concentration of PAHs in gas phase ranged from 31.4 to 84.7 ng

m^{-3} with nonobservable seasonal variation. Conversely, maximum PAH concentrations in the particulate phase occurred during winter months. Particulate concentration varied from 11.4 to 44.9 ngm^{-3}, with an average of 25.2 ngm^{-3}. PAH distribution between gas and particulate phase was in agreement with the sub-cooled vapor pressure. Shift in gas-particle distribution due to difference in ambient temperature elucidated to some extent the seasonal variation of the concentration of PAHs in particles (Tsapakis and Stephenou, 2005).

Atmospheric PAHs were determined in two places in a suburban area of Athens during June and November 2003. The total concentration in the gas phase ranged between 6.89 and 124 ng m^{-3}, while in the particulate phase between 0.44 and 13.2 ng m^{-3}. Maximum concentrations of the total PAHs (gas and particulate phase) were observed during the cold period with an average of 40.7 ng m^{-3}. PAHs were correlated with NO, NO_2 and O_3, wind speed, wind direction and temperature. Positive correlation was observed between PAHs and NO, NO_2, while negative correlation was detected between PAHs and O_3. The most abundant members were Phenanthrene, Anthracene, Fluorene, Fluoranthene and Pyrene. Potential sources of PAHs in aerosols were diesel and gasoline engines, although other sources such as coal combustion and liquefied petroleum gas also contributed (Vasilakos *et al*., 2007).

In India PAH concentrations have been monitored at various locations with a view to evaluate the carcinogenic risk from PAH exposure, such as Mumbai (Kulkarni 1997, Kulkarni and Venkataraman, 2000), Calcutta (Chattopadhyay *et al*., 1998), Lucknow (Bhargava *et al*., 2004 Pandey *et al*., 2013), Ahmedabad (Aggarwal *et al.*, 1982; Raiyani *et al.*, 1993), Delhi (Sharma *et al*., 2007a, 2007b, 2008; Singh *et al*.,2010, 2011, ; Gadi *et al* 2012), Chennai (Mohanraj *et al*., 2011a), Trichirrapalli (Mohanraj *et al*., 2011b), Coimbatore (Mohanraj *et al*., 2012), Agra (Dubey *et al*., 2014 ; Rajput and Lakhani, 2009, 2010, 2012; Singla *et al*., 2012; Masih *et al*., 2006, 2010) Studies carried out by Raiyani *et al*., (1993) in Ahmedabad showed total PAH concentration of 90 - 195 ng m^{-3} in an industrial area and between 23 - 66 ng m^{-3} in a residential area. Concentration of

four PAHs in a Mumbai industrial area (Pandit *et al.*, 1996) ranged between 20- 95 ng m^{-3}. PAH concentration in residential, commercial and industrial areas in Nagpur were 125 - 190 ng m^{-3} with over 70% of the mass in particles less than 10 µm diameter (Vaishali *et al.*, 1997). Atmospheric concentrations of polycyclic aromatic hydrocarbons (PAHs) in Delhi were evaluated to study particulate PAHs profiles during the different seasons of 2003 (Sharma *et al*., 2008). The annual average concentrations of total PAHs were found as 1,049.3 ng m^{-3} at Okhla, 1,344.37 ng m^{-3} at Daryaganj, and 1,117.14 ng m^{-3} at Dhaulakuan. The seasonal average concentrations were found to be maximum in winter and minimum during the monsoon season. Diesel and gasoline driven vehicles were identified as the principal sources of PAHs at all the three sites under investigation besides stationary combustion sources such as cooking fuel combustion and industrial emission. Airborne $PM_{2.5}$ and PAHs (sum of 9 PAHs) at Tiruchirappalli (202.6-333.7 ng m^{-3}) and Chennai (325.7 to 790.8 7 ng m^{-3}) observed to be at alarming levels (Mohanraj *et al*., 2011 a, b). Highest concentration of PAHs was observed during northeast monsoon season and lowest in southwest monsoon). Low and medium molecular weight PAHs such as Phenanthrene, Anthracene, Benzo(a)Anthracene and Chrysene were observed in all seasons. Principal compound analysis revealed gasoline and diesel vehicular emissions as major sources for PAHs compounds. Concentrations of PAHs at several sites in Agra have been observed to be high exhibiting greater concentrations in winter than summer in Total Suspended Particulate Matter (TSPM) (Rajput and Lakhani, 2009, 2010, 2012 and Lakhani, 2012) and PM_{10} and $PM_{2.5}$ (Singla *et al*., 2012) at Agra. The major sources are vehicular exhausts, coal and biomass combustion. Preliminary study on mutagenicity assessment of respirable particulate matter (PM_{10} and $PM_{2.5}$) revealed a potential for both base pair substitution and frame-shift mutagenicity (Singla *et al*., 2012) PAHs concentration in particulate and gas phase was investigated in indoor and outdoor air of urban residential and roadside homes in Agra (Masih *et al*., 2012). In particulate phase at roadside homes the annual mean concentration of PAHs in indoor was 5.53 to 952.28 ng m^{-3} in outdoor it ranged 15.47 to 1036.79 whereas at urban residential homes the particulate PAHs concentration range was 4.10 to

826.73 ng m^{-3} (indoor) and 8.32 to 826.73 ng m^{-3} (outdoor). The annual mean concentration of gaseous phase PAHs ranged from 2.75 to 90.34 ng m^{-3} indoors, 2.29 to 113.56 ng m^{-3} outdoors at roadside homes. In urban residential homes it ranged 2.64 to 87.58 ng m^{-3} in indoor, 4.79 to 51.83 ng m^{-3} in outdoor respectively. Significant seasonal variations of total PAHs concentrations were observed with higher levels during winter season. Cooking, smoking, incense burning were identified to be the indoor sources of PAH whereas in outdoor petrol and diesel combusted fuel and diesel exhaust from generator sets were the major sources. The concentrations of sixteen polycyclic aromatic hydrocarbons (PAHs) and trace metals adsorbed to respirable particulate matter (PM_{10}) and the fine fraction of particulate matter ($PM_{2.5}$) were determined in Delhi (India) during the winter and summer periods in 2007-2008 Total PAH concentrations for PM_{10} and $PM_{2.5}$ were much higher in winter (81.5 and 96 ng m^{-3}, respectively) compared to summer (33.1 and 45.8 ng m^{-3} , respectively) with high molecular weight homologues (4-6 ring PAHs), which account for 80-95.8% of total PAHs. In general, the $PM_{2.5}$ PAH concentrations were higher than PM_{10} particles (Gadi *et al*., 2012).

Few studies have also been conducted on determining emission rates of PAH from several combustion sources.PAH concentrations in indoor studies from Lucknow were found high for cow dung cake combustion ranging from 2.23 – 46.07 μg m^{-3} and lowest for LPG combustion ranging from 0.86 – 4.76 μg m^{-3} (Bhargava *et al*., 2004). Higher concentrations of PAHs were found in the breathing zones and maximum concentrations were obtained in winter compared to summer. Emission factors and Mutagenicity potential of PAH have also been determined for cowdung cakes, coal and fuel wood (Rajput *et al*., 2010), diesel fuel and diesel exhaust emissions from diesel generator (Rajput *et al*., 2009; Jain *et al*., 2012). Emissions were found maximum for cowdung cakes, while studies on diesel exhaust emissions revealed that high molecular weight PAH compounds are generated during the combustion process. Further the emissions showed a greater mutagenic potential for base pair substitution. Recently, the emission factors for particulate-phase

polycyclic aromatic hydrocarbons (PAHs) were evaluated for various biomass fuels (fuelwood, dung cakes, and agricultural residue) that are being commonly used in Delhi as a source of energy (Gadi *et al*., 2012). Emission factors of total particulate PAHs varied from 35.9 ± 1.9 to 59.7 ± 4.4 mg/kg. Fluoranthene, Pyrene, Benzo[a]anthracene, Chrysene, Benzo[b]fluoranthene, and Benzo[a]pyrene constituted the major fraction of PAH emissions from all biomass fuels.

OBJECTIVES

Despite their environmental relevance, only few studies have been conducted on PAH levels in atmosphere in Agra. These studies have only concentrated on the particulate phase concentrations and estimations of their carcinogenic risks. No study has been reported on the derivatives of PAHs and the partitioning of these compounds in the gas and particulate phases. Hence this study has been planned to determine

1. The gas and particle phase concentrations of PAHs in an urban area where heavy traffic exists and at a rural area with minimum anthropogenic activity.

2. Investigate the temporal and spatial changes in the gas and particle phase concentrations.

3. Apply the available gas - particle partitioning approaches to the data and determine the dominant partitioning mechanism for the sampling sites during the sampling period.

4. Assess the relationship between PAHs and ambient Ozone, NOx and Organic and Elemental Carbon concentrations as an indicator of photochemical activity.

5. Evaluate the origins of PAHs and nitro-PAHs in the air.

PROPOSED METHODOLOGY

SAMPLING SITES:

Samples will be collected from two sites in Agra, i.e from a rural and a traffic site. It is proposed to collect samples from Jairam ke Nagla, a small village near Malpura, Agra. It is an agricultural area with a very low population density. Traffic is also very scarce. Samples will also be collected near Bhagwan Talkies Crossing, National Highway Number 2, Agra, representing the traffic site. It observes dense mixed vehicular traffic throughout the day and night. The site is also a major residential and commercial area of the city which adds to a further traffic load.

SAMPLING:

Samples will be collected on quartz fibre filters (QFF) and on Poly urethane foam (PUF) plugs for both the particulate phase and gas phase respectively by High Volume Sampler Model TE-1000X (TISCH International, USA). The samplers will be operated at a constant flow rate, each sample will be of 24 hr duration. Sampling will be conducted simultaneously at both the sites twice a week. Prior to sampling, QFFs will be baked at 450 °C overnight and stored in aluminum foil packages until used. Before and after sample collection filter papers will be placed into desiccators at room temperature for 24 h to reach a constant humidity and weighed by a microbalance (Mettler AJ 150) to calculate particle mass concentrations. After weighing, the filter papers will be packed with aluminum foil and stored in a freezer. Poly urethane foam (PUF) plugs will be transported to the field without allowing exposure to ambient air and placed into containers after sampling and stored in a freezer until analysis.

EXTRACTION:

QFFs will be cut into small pieces and extracted twice with 50 mL mixture of dichloromethane and n-hexane in a ratio of 4:1 in an ultrasonic bath for 30 min at room temperature. The organic extract

will be filtered by using filter papers and will be cleaned employing a silica gel column. The extracts will be combined and concentrated to 2 mL using a rotary evaporator (300 mbar, 40°C). The PUF plugs will also be extracted in the mixture of dichloromethane and n-hexane by ultrasonication or by soxhlet extraction, the extract will be filtered and concentrated upto 2 mL and stored in deep freezer until analysis.

ANALYSIS:

16 PAH compounds and nitro-PAHs compounds will be analyzed in the extracts of filters as well as the PUF plugs by Gas Chromatography coupled to a Mass Spectrometer (GC-MS) equipped with a FID detector. Separation would be achieved on a 30 m, 0.25 mm internal diameter with 0.25 μm film thickness capillary column with stationary phase of dimethyl polysiloxane. Helium gas will be used as a carrier gas and temperature gradient programme will be used. Organic and Elemental Carbon content would be determined by the carbon analyzer after standardization by sucrose solution.

MONITORING OF OZONE, NO_X AND METEOROLOGICAL PARAMETERS:

Ozone and NOx would be monitored by online analyzers while the meteorological parameters like temperature, solar intensity, Relative humidity, wind speed and wind direction will be recorded by weather station (WM 271).

INTERPRETATION:

Statistical methods will be applied to assess seasonal and spatial variations, source identification, influence of meteorological parameters on PAHs concentrations, their gas and particle distribution and different models will be applied to assess the dominant portioning mechanism.

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